Summary

Thermodynamic functions for $Si(OH)_4(g)$ and $SiO(OH)_2(g)$ have been measured using the transpiration method. A second law enthalpy of formation and entropy and a third law enthalpy of formation has been calculated for $Si(OH)_4$. The results are in very good agreement with previous experimental measurements, *ab-initio* calculations, and estimates.

Thermodynamics of the Si-O-H System

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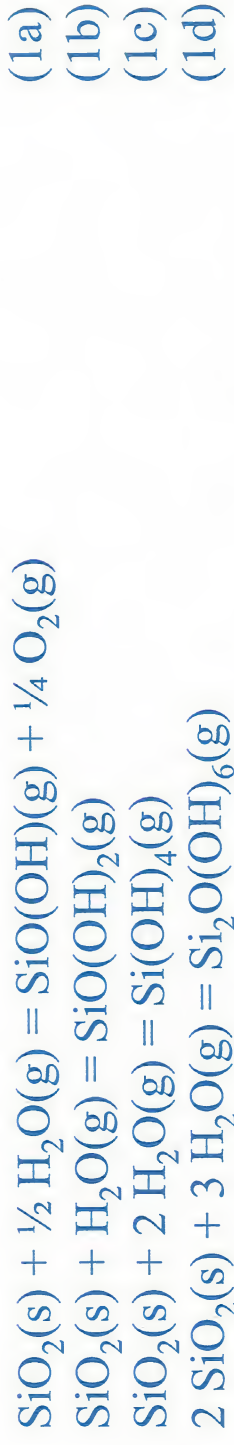Case Western Reserve University/NASA Glenn Research Center
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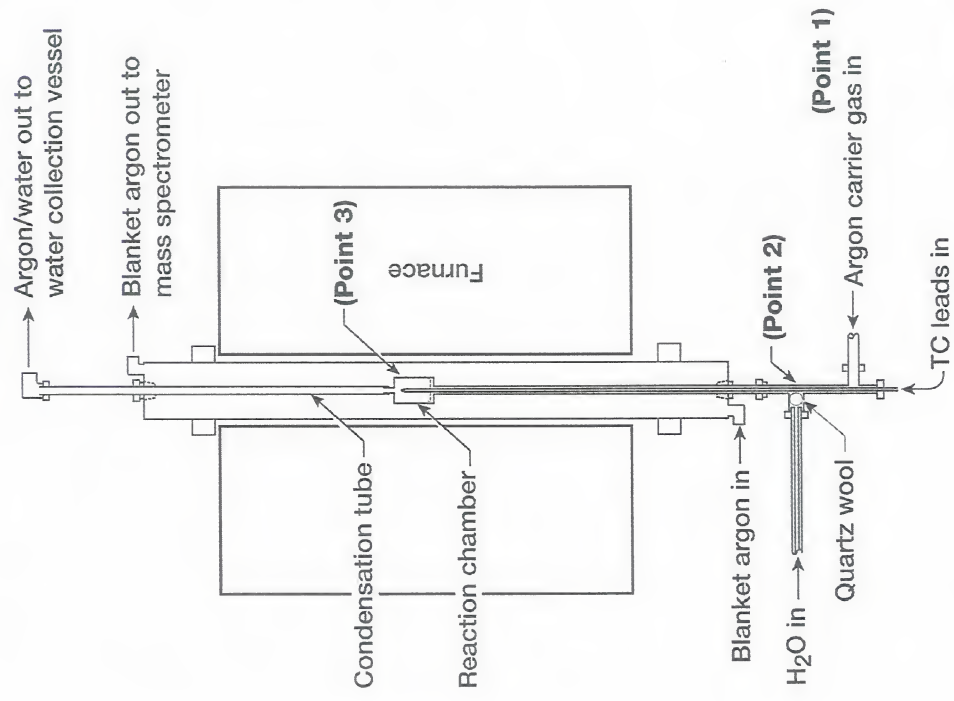
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Introduction

Silicon-oxygen-hydrogen gas phase species are important in a variety of applications, including high temperature corrosion of SiO_2 forming alloys and ceramics in water vapor containing environments.[1-3] Measurements of the pressures of Si-O-H species have been made using a transpiration apparatus similar to the design of Hashimoto.[4,11] The system can be used to provide flowing atmospheres of oxygen or argon with variable partial pressures of water. Samples of SiO_2 were placed in a Pt-20%Rh cell and heated from 900-1450°C. Volatile silicon hydroxides were transported by gas flow to the cooler condenser tube connected to the outlet nozzle and collected for chemical analysis.
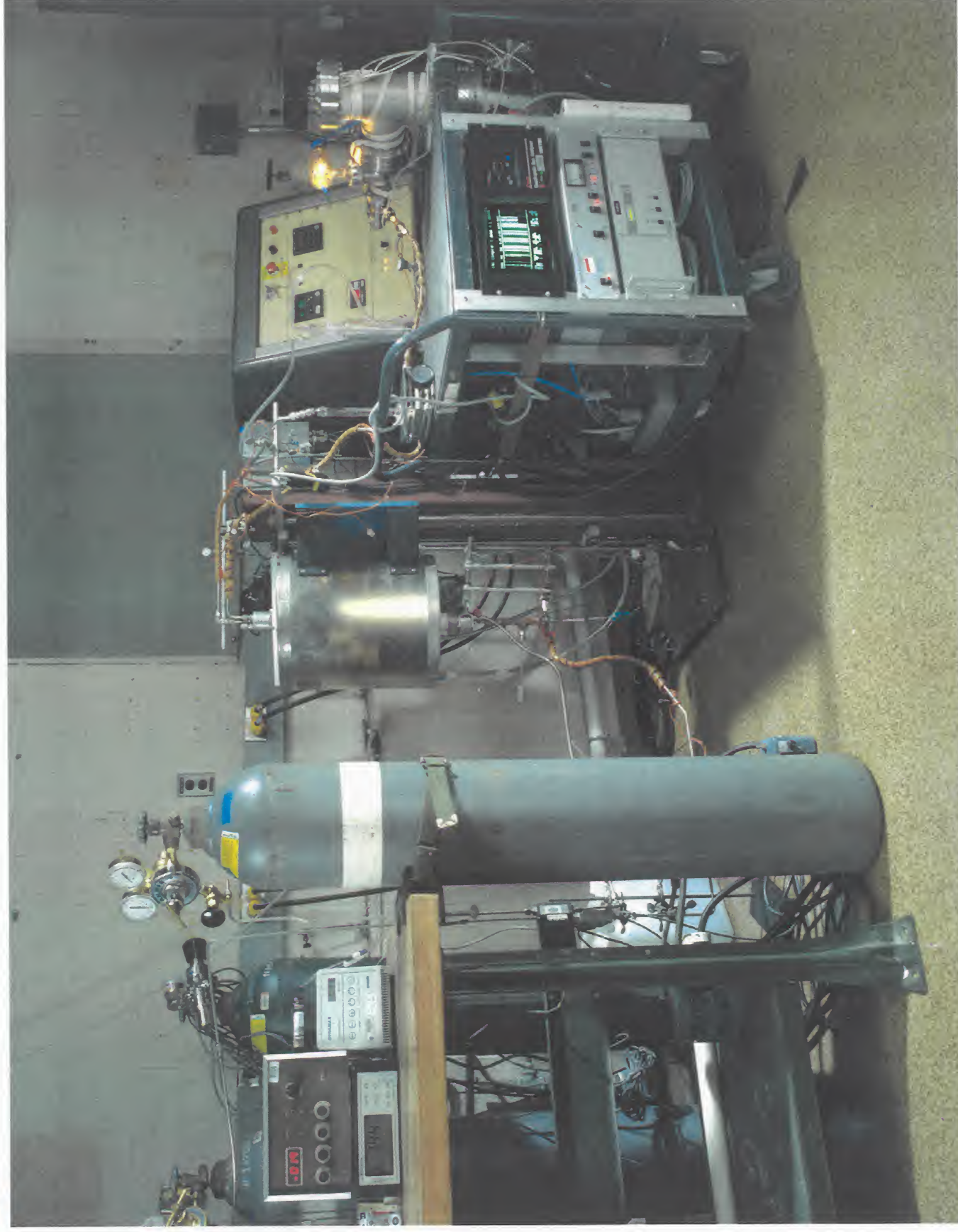
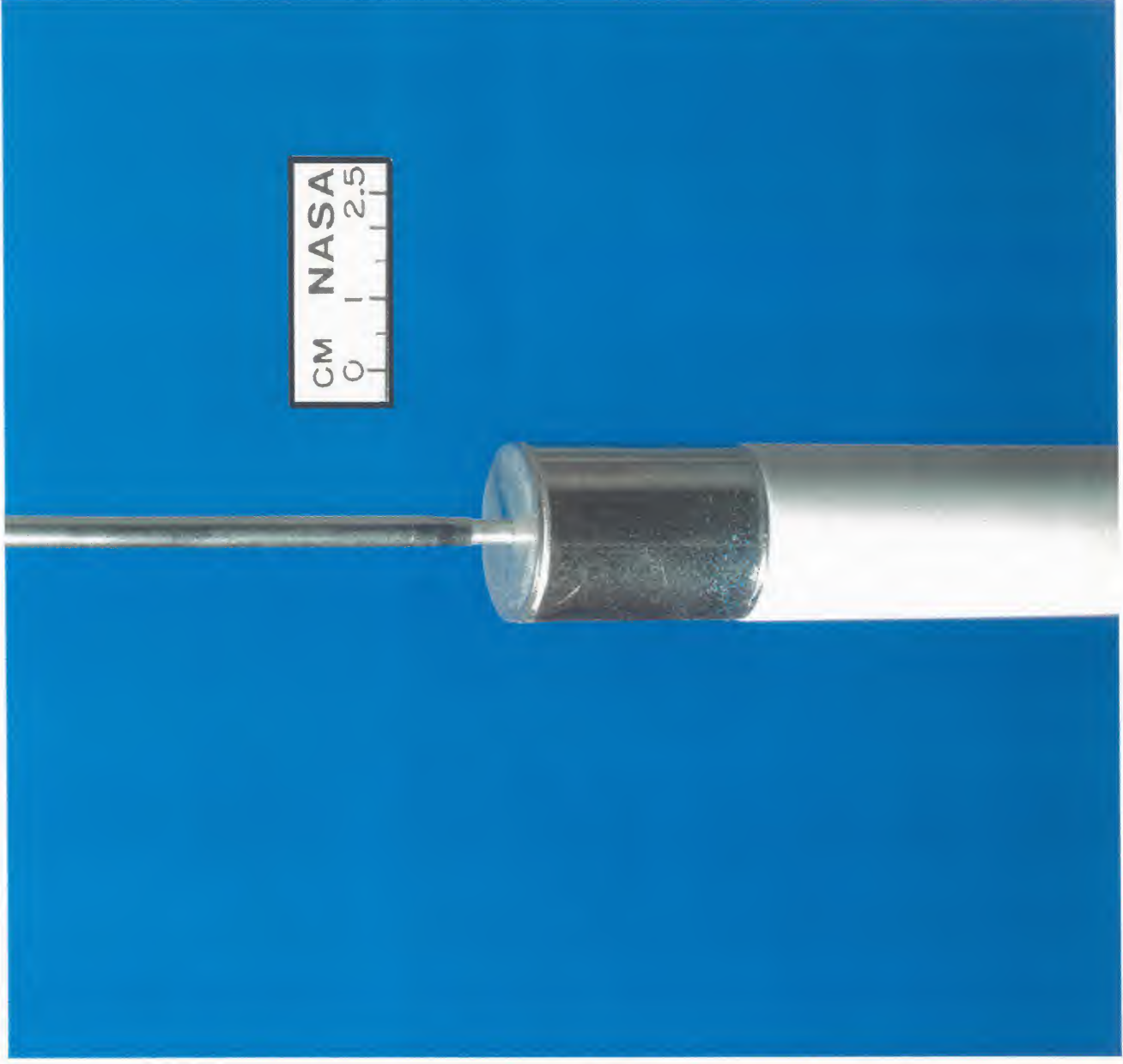Previous studies suggest the following reactions are important in the formation of silicon hydroxides and oxy-hydroxides:[5-9]

$SiO_2(s) + \frac{1}{2} H_2O(g) = SiO(OH)(g) + \frac{1}{4} O_2(g)$ (1a)

$SiO_2(s) + H_2O(g) = SiO(OH)_2(g)$ (1b)

$SiO_2(s) + 2 H_2O(g) = Si(OH)_4(g)$ (1c)

$2 SiO_2(s) + 3 H_2O(g) = Si_2O(OH)_6(g)$ (1d)

Allendorf et al.[6,7] report theoretical heats of formation at 298.15 K and Gibbs free energies of formation for a range of Si-O-H gaseous species. Free-jet expansion sampling mass spectrometry was used to study the interactions of SiO_2 with water vapor.[10] Clear evidence of $Si(OH)_4(g)$ as well as some evidence of $SiO(OH)_2(g)$ was seen.

Figure 1. Schematic of transpiration apparatus

Argon/water out to water collection vessel

Blanket argon out to mass spectrometer

(Point 3)

Furnace

Condensation tube

Reaction chamber

Blanket argon in

H_2O in

Quartz wool

(Point 2)

(Point 1)

Argon carrier gas in

TC leads in

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Flow and Pressure Calculations

The amount of Si containing condensate was converted to pressures by considering the flow rate of the argon carrier gas, water vapor, and the Si vapor species[4]. Consider first the molar flow rate of Ar, Q_{Ar}, entering the furnace (Figure 1, point 1) before water is introduced:

$$Q_{Ar} = \frac{P_1 f_1}{RT_1}$$

Here P_1 is the pressure, f_1 is the volume flow rate, R is the gas constant, and T_1 is the absolute temperature. The volume flow rate entering the reaction chamber (point 2) is given by

$$f_2 = \frac{T_2}{P_2} R[Q_W + Q_{Ar}]$$

Here Q_W is the molar flow rate of water. The volume flow rate leaving the reaction chamber (point 3) is the above expression with the addition of Q_{Si}, which is small in comparison to $Q_W + Q_{Ar}$, so we can take $f_3 = f_2$. The pressure of Si-containing species leaving the reaction chamber (point 3) is given by:
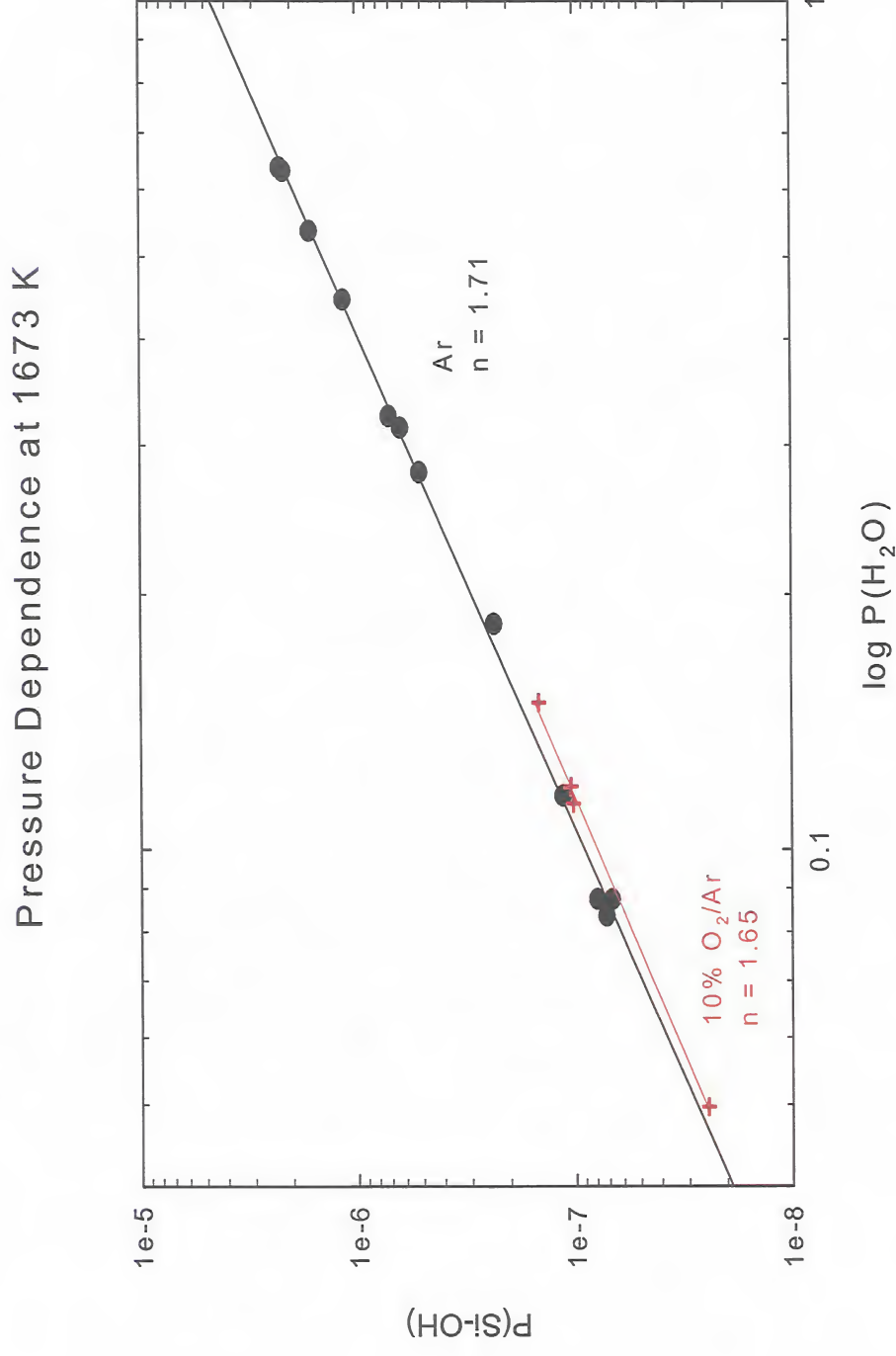
$$\frac{P_{Si}}{P_T} = \frac{Q_{Si}}{Q_{Ar} + Q_W + Q_{Si}}$$

or

$$\frac{P_{Si}}{P_T} = \frac{Q_{Si} RT_3}{f_3}$$

Figure 2. Dependence of the Si-O-H species pressure on P(H₂O).

Figure 2. Dependence of the Si-O-H species pressure on P(H_2O).
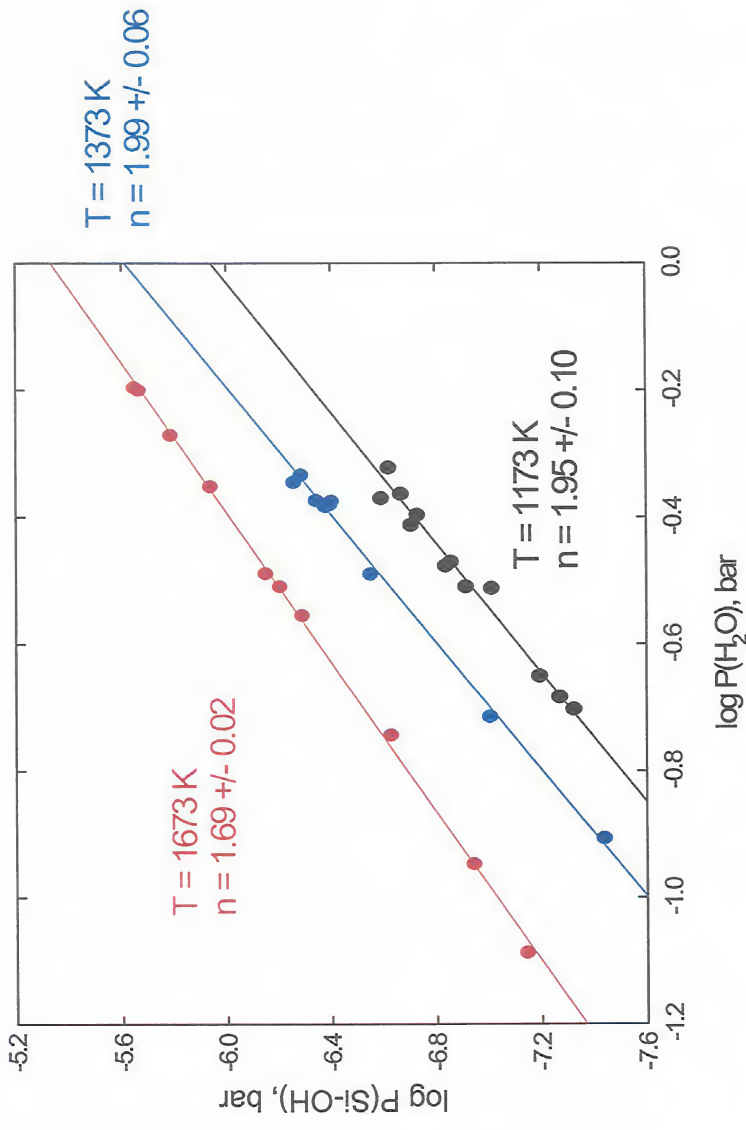
$P(H_2O)$ dependence < 2 at higher temperatures suggests an additional reaction besides 1c is important at these temperatures.
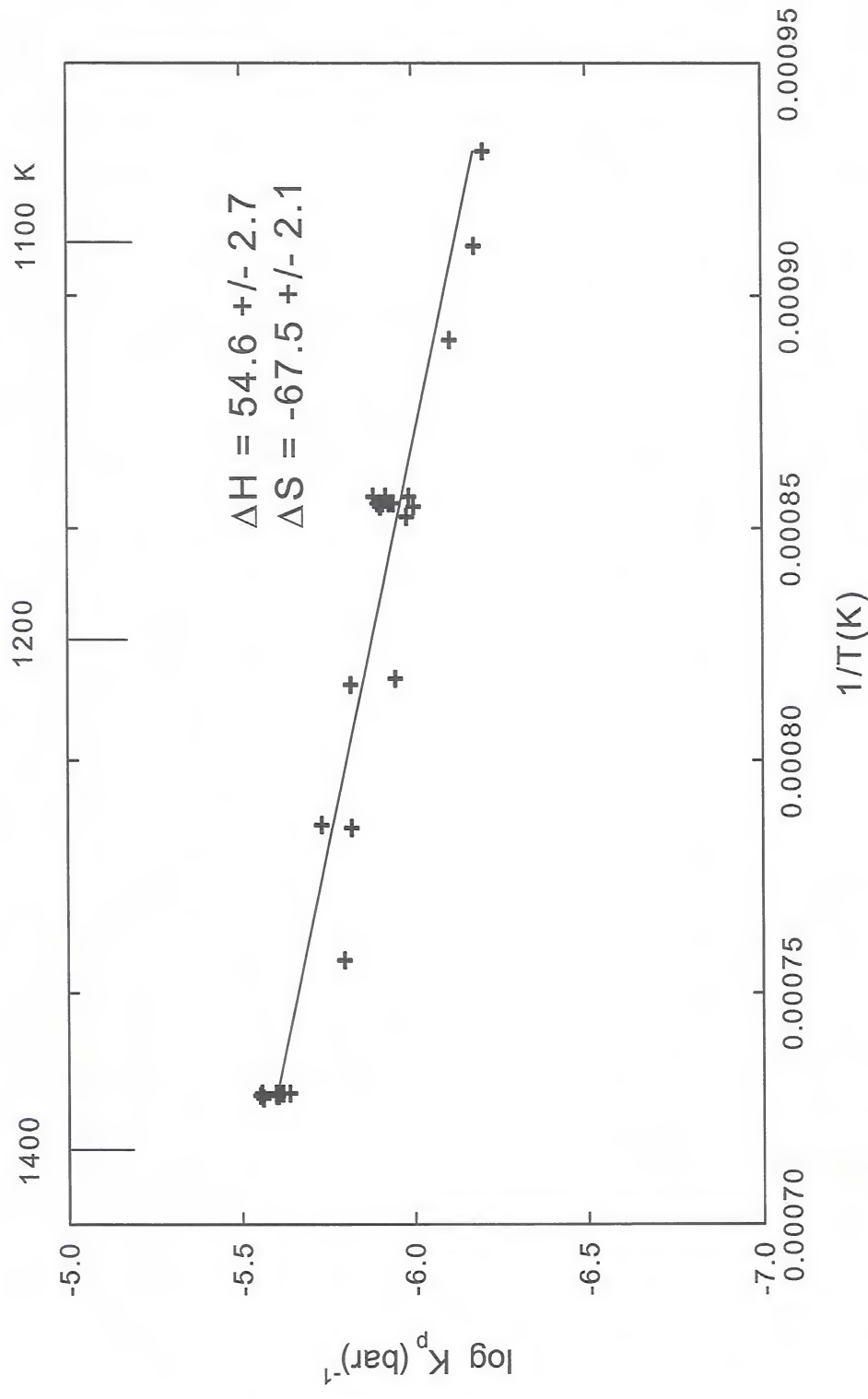
Figure 3. Effect of oxygen on P(Si-OH) at 1673 K.

Pressure Dependence at 1673 K

Lack of P(O₂) dependence indicates reaction 1a is not important.

Figure 4. Temperature dependence below 1673 K
for the reaction
$SiO_2(s) + 2H_2O(g) = Si(OH)_4(g)$

$\Delta H = 54.6 +/- 2.7$
$\Delta S = -67.5 +/- 2.1$

The calculations of Allendorf et al.[6,7] allow the derivation of the free energy function for a third law calculation of $\Delta_r H^o(298)$. Their thermal functions listed on the Web[7] can be used to extract the change in free energy function for the formation of $Si(OH)_4$ or $\Delta_f FEF^o(298)$. Using JANAF[12] data for Si, O_2, and H_2 the $FEF(Si(OH)_4)$ is determined to be:

$$FEF \ (\ Si \ (\ OH \ )_4 \ ) = \ \ 291.214 \ \ \ - 0.056846T \ \ \ \ \ \ \ \ + \ (\ 6.6727 \ \ \ x \ 10^{-6} \ )T^{\ 2}$$

$$- \ 32123.721/ \ \ \ T \ - \ 89.8145 \ \ \ ln(T)$$

This was used with the standard third law equation to calculate an enthalpy of reaction for reaction (1c):

$$\Delta_r H^o(298) = \Delta G^o(T) - T\Delta\left(\frac{G^o(T) - H^o(298)}{T}\right) = \ RTlnK_p - \ T\Delta(FEF^o(298))$$

See Table I for calculated enthalpies.

Table I. Calculated enthalpies of formation and entropies of Si(OH)$_4$(g)

Method	Investigator	$\Delta_fH(1200)$ (kJ/mol)	$S°(1200)$ (J/mol-K)	$\Delta_fH(1600)$ (kJ/mol)	$S°(1600)$ (J/mol-K)	$\Delta_fH(298)$ (kJ/mol)	$\Delta_fH(0)$ (kJ/mol)
Second Law	Hashimoto[4]			-1342.7 ± 2.7	592.5 ± 1.0		
Second Law	This study	-1354 ± 2.7	544.1 ± 2.1				
Third Law	Hashimoto[4,†]					-1344.1 ± 0.3	
Third Law	This study					-1344.1 ± 1.4	
Estimation	Krikorian[5]		511		563		-1348
ab-initio Calculations	Allendorf et al.[6,7]	-1342	539.47	-1339.9	587.21	-1342	

†FEF from Allendorf et al.[6,7]

Figure 5. Pressures of $SiO(OH)_2$ at 1673 K.
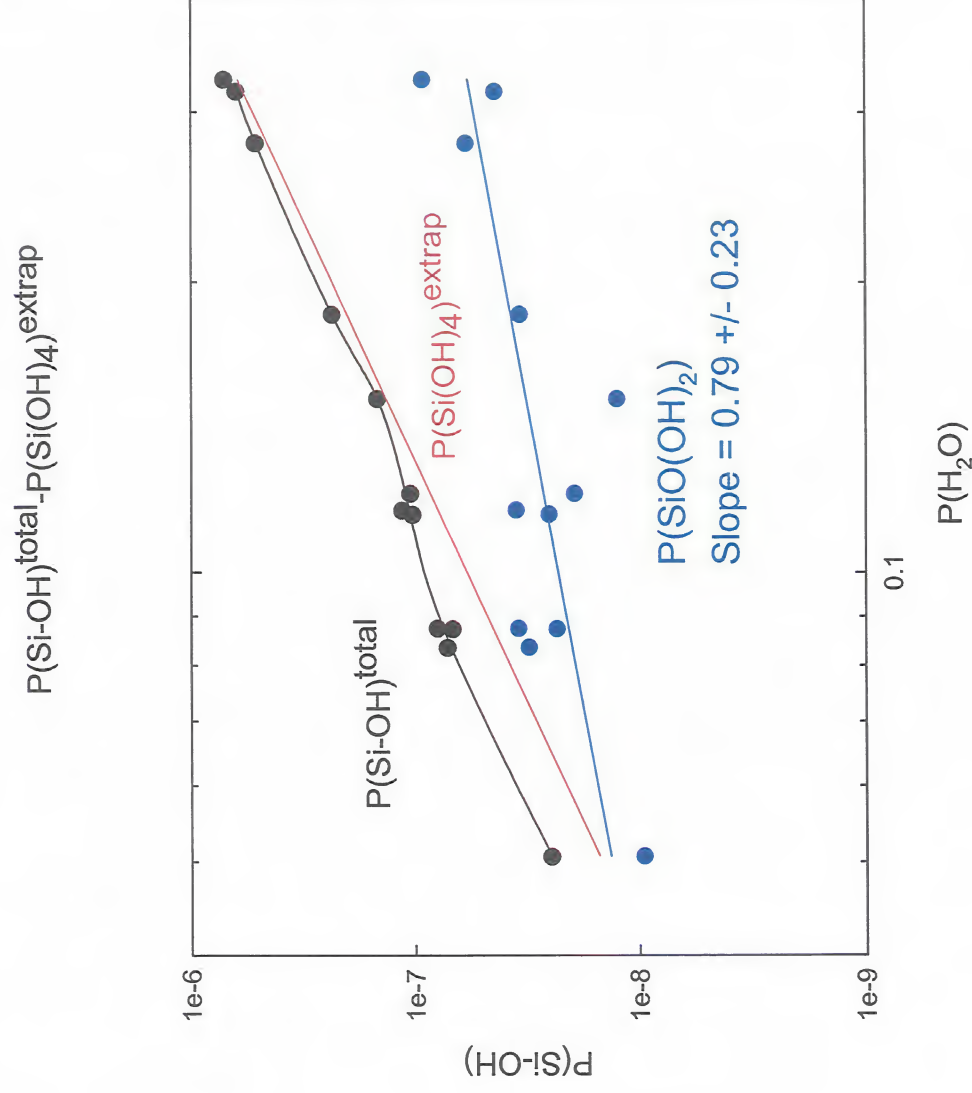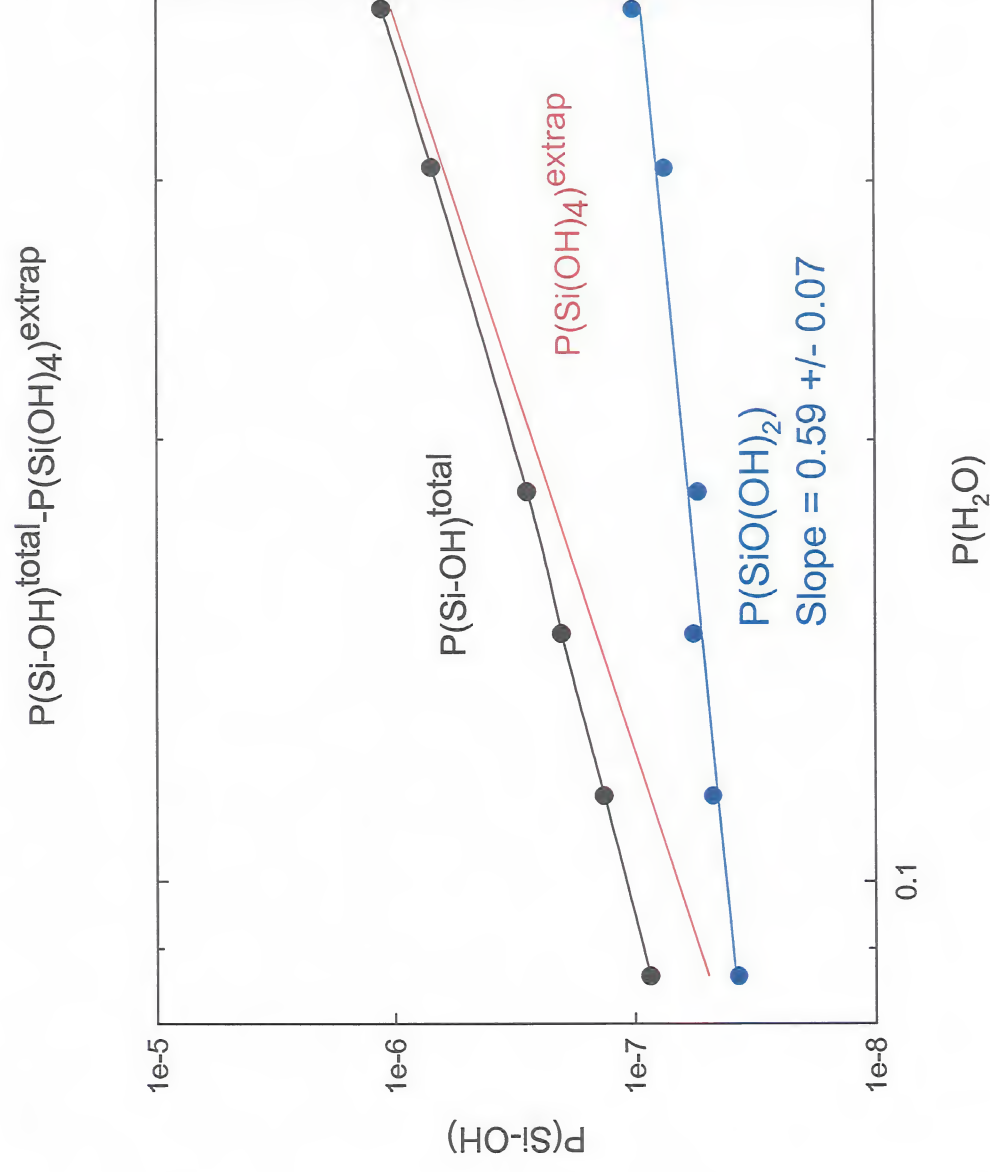
Figure 6. Pressures of SiO(OH)$_2$ at 1728 K.

The calculations of Allendorf et al.[6,7] were also used to calculate FEF(SiO(OH)$_2$). Using JANAF[12] data for Si, O$_2$, and H$_2$ the FEF(SiO(OH)$_2$) is determined to be:

$$FEF\ (SiO\ (OH\ )_2\ ) = \ 141.54\ - 0.039543T \quad + (\ 4.3293\ \ x\ 10^{-6}\ )T^2$$

$$- 21602T\ \ - 61.809\ \ ln(T)$$

See Table II for calculated third law enthalpies.

Table II. Enthalpy of formation of $SiO(OH)_2$ from this study and other studies.

Method	Investigator	Thermal Functions	$\Delta_f H°(298)$
Gas Leak Knudsen Cell	Hildenbrand and Lau	Estimated	-891.2 ± 16.7
Recalculated Gas Leak Knudsen Cell	Hildenbrand and Lau	Allendorf et al.	-811 ± 18
ab-initio Calculation	Allendorf et al.	Allendorf et al.	-755.7
Transpiration	This study	Allendorf et al.	-831 ± 5.1

Summary and Conclusions

Thermodynamic functions for $Si(OH)_4(g)$ and $SiO(OH)_2(g)$ have been measured using the transpiration method. A second law enthalpy of formation and entropy and a third law enthalpy of formation has been calculated for $Si(OH)_4$. The results are in very good agreement with previous experimental measurements, *ab-initio* calculations, and estimates.

At temperatures of 1673 and 1728 K, water vapor pressure dependent experiments suggest that a second vapor species is important. Lack of oxygen dependence suggests this species is $SiO(OH)_2$. By subtracting the extrapolated pressure of $Si(OH)_4(g)$ at 1673 and 1728 K, pressures of $SiO(OH)_2(g)$ are determined. These values were used in a third law analysis to obtain a heat of formation of $SiO(OH)_2$. Recalculation of gas-leak Knudsen cell third law data from Hildenbrand and Lau[8,9] using the thermal functions of Allendorf *et al.*[6,7] leads to a heat of formation of $SiO(OH)_2$ in reasonable agreement with the transpiration data of this study.